SCIENCE FOR CERAMICS PRODUCTION

UDC 666.76

OXIDE CERAMICS OF THE NEW GENERATION AND AREAS OF APPLICATION

E. S. Lukin,[1] N. A. Makarov,[1] A. I. Kozlov,[1] N. A. Popova,[1] E. V. Anufrieva,[1] M. A. Vartanyan,[1] I. A. Kozlov,[1] M. N. Safina,[1] D. O. Lemeshev,[1] and E. I. Gorelik[2]

Translated from *Steklo i Keramika*, No. 10, pp. 27 – 31, October, 2008.

The results of studies on production of modern ceramic materials with high performance properties are reported. The process features for creating a high-density, wear-resistant ceramic based on partially stabilized zirconium dioxide, aluminum oxide, a mixture of these oxides, dense and porous materials from aluminum, zirconium, magnesium oxides, silicon carbide, and a bioactive ceramic made from hydroxyapatite and tricalcium phosphate were examined. The prospects for using the new ceramic materials for solving modern scientific and industrial problems were demonstrated.

Modern ceramics technologies with a high level of performance properties — a new generation of ceramics developed in many countries in recent years, including in our country — must be considered advanced materials technologies. Several groups of ceramic materials that allow solving important scientific and industrial problems related to the development of new technology are the most promising.

Group I. ***High-density, strong, wear-resistant ceramic materials based on partially stabilized zirconium dioxide, aluminum oxide, and composites based on a mixture of these oxides.*** With the discovery of transformation strengthening of partially stabilized zirconium dioxide (PSZD), solving the problems of obtaining strong and ultrastrong ceramic materials was basically aimed at obtaining ceramics using PSZD and compositions with other oxides. Most of the leading countries came to be concerned with technology for fabricating items made of PSZD and studying their properties and areas of application. In addition to PSZD, ceramic materials of the $Al_2O_3 – ZrO_2$ system, in which zirconium dioxide is in the tetragonal modification (stabilizer: 3% yttrium, molar content) are widely used.

The flexural strength of the PSZD ceramic varies within wide limits — from 500 to 2500 MPa as a function of the powder fabrication technology, molding methods, and sintering conditions. The highest values of the flexural strength (up to 2000 – 2500 MPa) and crack resistance (over 15 MPa $\cdot$ m$^{1/2}$) are attained in sintering stock made of ultradisperse powders by hot isostatic molding [1]. Strength of 800 – 1000 MPa can be attained with ordinary sintering [2].

In addition to high strength and crack resistance, the advantages of ceramic materials made from PSZD are significant hardness, wear resistance, low friction coefficient combined with metals, and possibility of very high surface purity (R_z under 0.01 μm). Various thread guides and spinnerets, cutting and boring tools for processing metals and wood, balls for different applications, wear-resistant articles for any application, articles with different porosity, high strength, etc., are made from these ceramics.

The mechanism of transformation strengthening is only possible if crystals much smaller than 1 μm in size remain after firing (Fig. 1), since the tetragonal solid solution of yttrium oxide in zirconium dioxide is metastable. When the crystals are larger than this size, pronounced disordering takes place due to transition of the tetragonal phase into the monoclinic phase, i.e., a polymorphic transition with an increase in volume.

Due to these features of the microstructure of PSZD ceramic, one of the basic stages of the technology is preparation of ultrafine tetragonal zirconium dioxide powders.

[1] D. I. Mendeleev Russian Chemical Engineering University (RKhTU), Moscow, Russia.
[2] Russian Medical Academy of Post-Graduate Education, RF Ministry of Health.

0361-7610/08/0910-0348

A method for preparation of ultrafine PSZD powders was developed at the beginning of the 1980s in the Department of Chemical Engineering of Ceramics and Refractories at D. I. Mendeleev Russian Chemical Engineering University; it consisted of heterophase deposition of hydroxides from hot concentrated solutions of zirconium and yttrium salts in a solution of ammonia.

The use of special deposition conditions and mechanically active powders allows obtaining aggregates less than 0.1 μm in size that consist of particles several tends of nanometers in size (Fig. 2). A ceramic with flexural strength of up to 2500 MPa was fabricated from these powders using molding in a hydrostat and sintering in a gasostat at 1400 – 1500°C [4].

The special structure of PSZD powder determines the mechanism of sintering of samples prepared from this powder. The high concentration of defects and uncompensated chemical bonds between atoms ensures high mobility of the particles constituting the aggregates.

A detailed study of formation of the microstructure of the ceramic during sintering indicated the effect of a mechanism of diffusion-viscous flow in which the particles exhibit high plasticity, ensuring a nonporous material in any gaseous media.

In the first stage of sintering, aggregates 0.1 – 0.2 μm in size draw together until totally in contact due to surface tension forces and then begin to move into the pore volume where they must change shape in order to "line up" next to each other according to the minimum energy principle. However, the aggregate must initially be converted into a crystal due to the constituents of its nanoparticles, which can easily change their coordinates in the bulk of the entire aggregate. If the position of the particles changes in viscous flow, their crystal lattice will coincide with the crystal lattice of neighboring particles and they will coalesce, which in the final analysis causes the formation of a single crystal from the aggregate.

As a consequence, the smaller the aggregates, the smaller the size of the crystals formed from them in the intermediate stages of sintering.

Subsequent alignment requires alteration of the shape of the crystals formed, which is ensured by the high level of defectiveness of the crystal lattice in the bulk and on the surface of the crystals. The high concentration of vacancies on the surface and segregation of the small number of contaminants in the boundary surface layers of the crystals cause melting of the substance in the thin boundary layer, which improves the conditions for slipping of the crystals. The concentration of vacancies in bulk due to formation of a solid solution of Y_2O_3 in ZrO_2 and nonuniformity of the stresses that arise simultaneously alter the shape of the crystals due to bulk diffusion.

Movement of aligned crystals under the effect of surface tension forces causes them to fill the pore volume and consequently densification of the sintered stock.

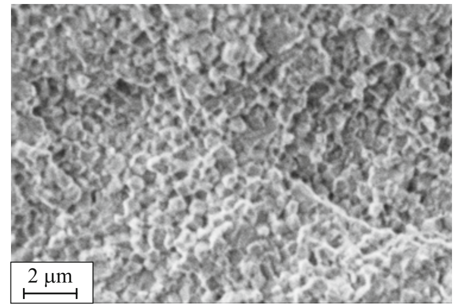

Fig. 1. Microstructure of PSZD ceramic (chip).

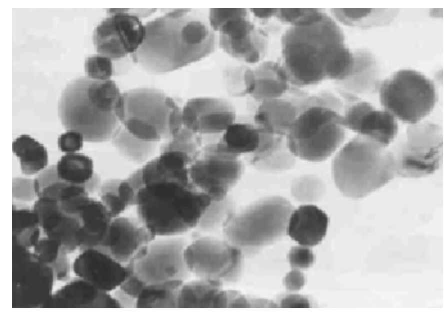

Fig. 2. Structure of PSZD powders obtained by heterophase deposition (× 180,000).

The densification process takes place without significant recrystallization, and the crystals themselves can turn and coalesce with neighboring crystals when the crystallographic lattice parameters coincide during such movement. Crystal growth can only take place when they almost totally fill the pore volume, i.e., when movement ends. An almost nonporous material with an initial aggregate size that is converted into individual crystals during firing, determined by the previous history of the powder used. By adjusting the firing conditions, the size of the crystals in the ceramic can be further controlled.

For PSZD, the firing conditions must ensure obtaining a nonporous ceramic with a maximum crystal size of 0.7 – 0.8 μm, which gives it high strength. At a 1.0 – 1.2 μm crystal size, the T → M transition takes place with an increase in the volume, which sharply weakens the ceramic.

The described sintering mechanism takes place in production of a transparent ceramic and other types of oxide ceramics made from nanopowders.

Group II. ***New dense ceramic materials made from aluminum oxide.*** Dense corundum ceramics with many favorable properties required for fabrication of different articles: high mechanical strength, hardness, wear resistance, refractoriness, thermal conduction, and chemical stability, are most widely used in domestic and foreign practice for many areas of technology.

A large number of high-quality materials made from corundum has been created for electronics and electrical engineering and for construction applications. The best known

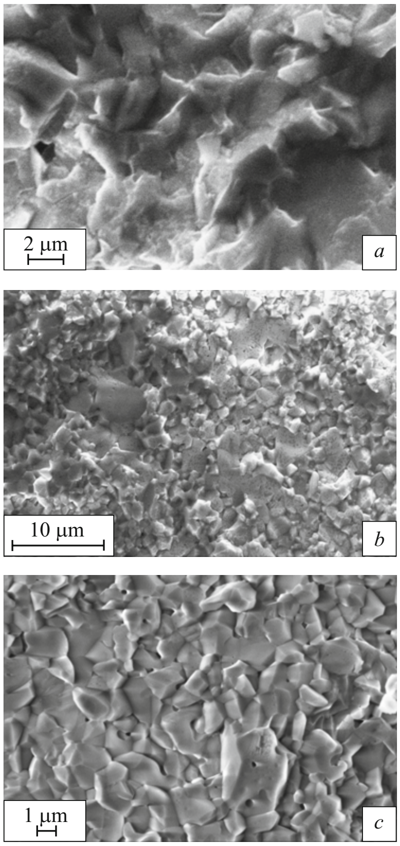

Fig. 3. Microstructure of ceramics of the $CaO – B_2O_3 – Al_2O_3$ system (*a*), Rubalite ceramic (*b*), and Almatis Co. ceramic made from alumina (*c*).

and most widely used in industry are VK-94-1, VK-100-1, TsM-332 (microlite), kartinite, sicor, coral-2, and many others. They are characterized by different microstructure, phase composition, and properties.

Studies of the technology, properties, and performance of corundum articles showed that almost nonporous articles with a finely crystalline and uniform structure are the most suitable for the majority of areas of technology. The strength parameters of corundum materials vary within 300 – 750 MPa as a function of the type of additives and methods of fabrication of the articles. Strength at the 700 – 750 MPa level can be attained with highly disperse powders and sintering of the articles by the hot molding method or in a gasostat [5]. Using ordinary sintering of industrial types of aluminum oxide produces articles with a flexural strength of 300 – 450 MPa [6, 7].

Many studies on fabrication of corundum ceramics with addition of eutectic compositions of different systems have been conducted in recent years, and their effect on sintering and formation of the structure and properties of the ceramics are being studied. A feature of these additives is that the amount that efficiently acts on these processes is 0.5 – 5.0%.[3] The effect of the additives is based on formation of a small amount of eutectic melt that actively participates in sintering. On cooling, the melt crystallizes, so that ceramics with these additives contain no glass phase. Additives of the systems $MnO – Al_2O_3 – SiO_2$, $MnO – TiO_2$, $MgO – SiO_2$, $MgO – TiO_2$, and some others, which allow decreasing the sintering temperature in air medium from 1700 – 1750 to 1300 – 1550°C, can be distinguished. Dense finely crystalline materials with a high level of properties and flexural strength of 300 – 400 MPa are obtained. Additional incorporation of disperse PSZD powder makes it possible to increase the strength of the ceramic to 550 – 600 MPa at a sintering temperature of 1450 – 1500°C.

We investigated the effect of approximately 15 compositions of eutectic additives with a eutectic point of 1115 – 1500°C. They all effectively act on sintering of corundum ceramics to a highly dense state at a reduced temperature. The corundum ceramic with the added eutectic compositions can be widely used in different areas of technology. In addition to high strength, these materials are characterized by important wear resistance and surface purity after grinding and polishing [8].

The areas of application are: electrical insulators, spark plug insulators, linings for cutoff valves, grinders, sealing rings in pumps, balls and plungers in pumps, vacuum tight ceramics for metal ceramic parts, tension rings for drawing machines, etc.

New areas of application of ceramic materials are the telecommunications industry and automobile, space, and aviation sectors, which raise the problem of developing new ceramic materials for supports for electronic microcircuits, electronic components, for packaging of assembled electronic modules, and other items with similar applications. Special attention is being focused on the creation and use of ceramic articles with a high sintering temperature which can be made with high-quality powders and low-temperature firing technology. Use of Sitall ceramics made from aluminum oxide, in particular, with additives of the $CaO – B_2O_3 – Al_2O_3$ system, for fabricating such items is also indicated [9].

At D. I. Mendeleev RKhTU, a dense (density of 2.4 – 2.5 g/cm^3 with zero closed porosity) ceramic of the indicated composition was made by synthesis from ultradisperse powders in the solid phase (Fig. 3*a*). The flexural strength of such material is 80 – 100 MPa and the dielectric constant is 8.2 in the frequency range up to 1 with zero closed porosity) ceramic of the indicated composition was made by synthesis from ultradisperse powders in the solid phase (Fig. 3*a*). The flexural strength of such material is 80 – 100 MPa and the dielectric constant is 8.2 in the frequency range up to 10^6 Hz.

One problem at present is to develop new ceramic materials for electrical engineering — a substrate for microcircuits and resistor bases. Except for Polikor ceramic, there are almost no other materials. Many organizations in Russia have recently used foreign supports made of Rubalite material manufactured from alumina by the German company Almatis (Fig. 3*b*). The size of the alumina aggregates recom-

3 Here and below: mass content.

mended for fabrication of articles in electrical engineering is 0.4 – 0.8 μm. Ceramics made of this material are sintered at 1500°C and have a density of 3.9 g/cm^3 and flexural strength of 300 MPa.

The structure of this alumina, the sintering kinetics in the 1250 – 1550°C range, and the structure and some properties of fired samples were investigated at D. I. Mendeleev RKhTU. The maximum density of the samples was 3.90 – 3.92 g/cm^3 and the flexural strength was 300 ± 30 MPa. The material was distinguished by the almost total absence of pores and had a crystal size of 2 – 3 μm (Fig. 3*c*). It is promising for fabrication of supports and resistor bases.

Group III. ***Strong porous materials made of aluminum, zirconium, magnesium oxides and silicon carbide for filters and membranes.*** These articles are characterized by a flexural strength of 50 – 100 MPa and higher, 30 – 50% porosity, a different pore sizes — from 1 to 100 μm and more. Application of a selective layer allows using the articles as membranes.

The advantages of these materials are: high strength, chemical inertness, different areas of application, multiple uses, use at high temperatures, and solution of the most important environmental problems.

The use of active highly disperse additives that ensure obtaining a given pore structure and high porosity and permeability for a given filler grain composition allows obtaining materials with porosity of up to 50 – 60% and flexural strength up to 50 MPa with a pore size of 5 – 10 μm and more at comparatively low firing temperatures (1250 – 1400°C).

A strong porous ceramic characterized by a pore size from micrometers to millimeters as a function of the method of fabrication can be made from compositions containing PSZD and are currently widely used for filtration of different gases and liquids and in catalytic processes. Materials with approximately 50% porosity, pore size less than 1 μm, and strength up to 200 MPa in sintering in air medium at 1000 – 1200°C are made from PSZD.

The use of actively sintered alumina with ZrO_2 additive allows fabricating strong porous materials (up to 40 – 50% porosity) and articles with high chemical stability for different filtering systems. Highly disperse PSZD and aluminum oxide powders are being successfully used for creating a selective layer on filter elements [10].

The basic areas of application are: purification and ozonation of drinking water, filtration of liquid food products (milk, wine, etc.), separation of liquids and gases, treatment of gases, treatment of petroleum product wastes, in medicine — separation of blood, storage of liquid drugs and their administration by absorption from the porous ceramic through the skin, production of ultrapure hydrogen with 10-fold savings of precious metals, etc.

An aluminum oxide ceramic with a honeycomb structure was created at D. I. Mendeleev RKhTU and is widely used as a catalyst support. The microstructure of this material is shown in Fig. 4.

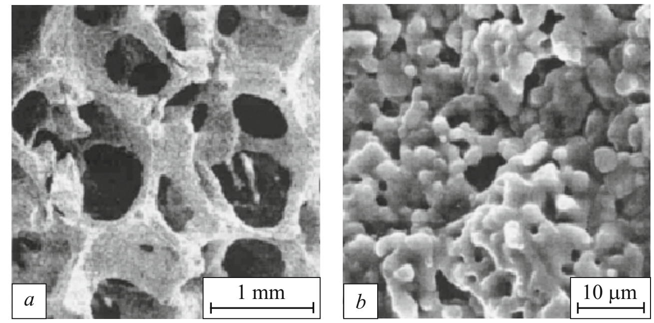

Fig. 4. Microstructure of aluminum oxide honeycomb ceramic: *a*) overall view; *b*) bridge.

A block, highly porous honeycomb catalyst [11] with the following properties was developed with this support: minimum porosity of 90 – 93%, microporosity under 30%, average pore diameter of 0.5 – 2.0 μm, compressive strength of 0.5 – 2.0 MPa. The pressure loss of the catalyst is 3 – 5 times less than for a granulated bed.

A method of catalytic hydrorefining of petroleum feedstock using hydrogen or a hydrogen-containing gas was developed, where block honeycomb material with a supported catalytically active component (nickel, palladium) whose surface is modified with nanoparticles is used as the catalyst. During the reaction, attrition of the catalyst does not take place and fragments of the catalyst are entrained with the reaction mass and as a consequence, fresh catalyst does not have to be added.

The number of process stages is reduced, since there is no need to separate the reaction mass from the catalyst particles, i.e., to filter it. No decrease in the activity was observed in regeneration of the catalyst (more than 50 times at a temperature of 550°C).

Use of the block honeycomb nanocatalyst allows obtaining gasoline with a maximum sulfur content of 6 ppm. In hydrotreating, not only is sulfur removed from petroleum products, but the color and odor also improve and the cetane number of diesel fuel increases.

Processes for reduction of aromatic mono- and polynitro compounds to the corresponding amines were developed using block honeycomb catalysts, hydrogenation of unsaturated hydrocarbons and nitrile rubber and hydrogenation and disproportionation of resin were conducted.

Superacid honeycomb catalysts allow conducting nitration of aromatic compounds with nitric acid alone.

Group IV. ***Ceramic bioactive materials made of hydroxyapatite and tricalcium phosphate.*** These materials are primarily used in medicine (stomatology, replacement and reconstructive-restorative surgery) in the form of powders, granules, and dense and porous ceramics.

A strong porous ceramic was developed from hydroxyapatite at D. I. Mendeleev RKhTU. We fabricated a dense ce-

ramic from pure hydroxyapatite with zero porosity and up to 100 MPa flexural strength; it has been used at the Central Scientific-Research Institute of Stomatology in approximately 20 maxillofacial surgeries. In all cases, there were no complications related to rejection of the implant in the postoperative period.

A porous ceramic made of hydroxyapatite with high strength, up to 90% porosity, and 0.5 – 1.0 mm pore size was also created. This ceramic is easily processed mechanically and can be used in treatment of bone trauma. As a function of the requirements, the ceramic can be fabricated in different shapes and configurations. The porous bioceramic developed is used in clinical conditions as an implant for eliminating bone tissue defects [12]. Ten surgeries have been performed. Observations of the behavior of the implants in the body showed that they are converted into bone tissue over approximately one and a half years. The structural elements of the porous bioceramic are similar to the structure of the honeycomb ceramic (see Fig. 4).

Group V. *Optically transparent ceramics.* Transparent ceramics are a special class of ceramic materials characterized by the theoretical density and high light transmission in the visible and UV regions of the spectrum.

Ceramics from Y_2O_3, Sc_2O_3, $Y_3Al_5O_{12}$, and solid solutions based on them not only have high transparency but also a high melting temperature, no polymorphic transformations, good electrophysical properties, especially for yttrium – aluminum garnet, stability in alkali metal vapors, and high thermal stability [13].

The absence of porosity ensures a high-quality polished surface, while the light transmission of these materials extends the areas of application, in particular, use as the working element of a solid-state laser.

The problem is only that a highly transparent ceramic must be obtained without adding tetravalent cations, since their presence will extinguish laser radiation.

The combination of these oxides and formation of solid solutions between them allow obtaining high transparency in vacuum sintering at acceptable temperatures.

Highly disperse powders of monofractional composition with uniform distribution of components must be used to fabricate these materials. These powders can be successfully fabricated by a method of special chemical deposition, since it makes it possible to synthesize nanosize particles which are homogeneous in size and chemical composition.

REFERENCES

1. E. S. Lukin, N. A. Popova, N. I. Zdvizhkova, et al., "Production of a strong ceramic containing zirconium dioxide," *Ogneupory*, No. 3, 5 – 7 (1991).
2. S. Yu. Pliner, D. S. Rutman, A. A. Dabizha, et al., "High-strength ceramic made of tetragonal zirconium dioxide," *Ogneupory*, No. 9, 19 – 20 (1986).
3. E. S. Lukin, "A modern high-density oxide ceramic with an adjustable microstructure. Part IV: Process methods for manufacturing highly disperse powders for a multicomponent ceramic," *Ogneup. Tekh. Keram.*, No. 9, 2 – 10, (1986).
4. E. S. Lukin, N. A. Popova, V. Ganykirzh, et al., "High-strength ceramic in the $Al_2O_3 – ZrO_2 – Y_2O_3$ system," in: *Coll. Works of D. I. Mendeleev MKhTI and Prague Chemical Engineering Institute* [in Russian], Moscow (1990), pp. 17 – 19.
5. E. S. Lukin, N. A. Popova, D. L. Tsetskhladze, et al., "The strong corundum ceramic Sikor," *Ogneupory*, No. 3, 11 – 12 (1991).
6. V. L. Balkevich, *Industrial Ceramics* [in Russian], Stroiizdat, Moscow (1984).
7. E. S. Lukin, N. T. Andrianov, N. B. Mamaeva, et al., "The problem of fabricating an oxide ceramic with an adjustable structure," *Ogneupory*, No. 5, 11 – 15 (1993).
8. E. S. Lukin, N. A. Makarov, N. A. Popova, et al., "New types of corundum ceramics with eutectic composition additives," *Konstr. Kompozit. Mater.*, No. 3, 28 – 38 (2001).
9. M. A. Vartanyan, E. S. Lukin, and N. A. Popova, "Low-temperature firing ceramic for microcircuit substrates," *Steklo Keram.*, No. 11, 28 – 30 (2008).
10. E. S. Lukin, A. L. Kuteinikova, and N. A. Popova, "Porous, permeable aluminum oxide ceramic," *Steklo Keram.*, No. 3, 13, 17 – 18 (2003).
11. A. I. Kozlov, E. S. Lukin, I. A. Kozlov, et al., "Activity of a block honeycomb catalyst with a modified support," *Steklo Keram.*, No. 7, 12 – 14 (2005).
12. M. N. Safina, T. V. Safronova, and E. S. Lukin, "Ceramic based on calcium phosphates with low sintering temperature containing a resorbable phase," *Steklo Keram.*, No. 7, 19 – 24 (2007).
13. D. O. Lemeshev, E. S. Lukin, N. A. Makarov, et al., "Prospects for creating new optically transparent materials from yttrium and yttrium – aluminum garnet," *Steklo Keram.*, No. 4, 14, 19 – 25 (2008).